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Complexation of poly(monobenzyl itaconate) and poly(N-vinyl-2-pyrrolidone) in dilute solution, 2. Influence of variables involved in sample preparation

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SUMMARY:

Upon mixing dilute solutions of poly(monobenzyl itaconate)[b] (PMBI) and poly(*N*-vinyl-2-pyrrolidone) (PVP) in methanol, a soluble interpolymer complex is formed whose properties depend on the method employed to prepare the sample. It was found that the local concentration of the polyacid is the controlling factor. Depending on that concentration, a metastable polymer complex is formed which turns to equilibrium upon sonication. Cooling or heating and aging time have a minor effect. The turbidity of the polymer complex depends on the polyacid concentration to the power ν (at constant polybase/polyacid ratio). For the metastable complex, $\nu \approx 2$, typical of weak polymer complexes. Changes in turbidity are accompanied by a decrease in ν. In the equilibrium state, $\nu \approx 1{,}5$, a value being more typical of strong complexes.

Introduction

Interpolymer complexes have recently attracted much attention [1], due to the interest in preparing compatible polymer blends [2].

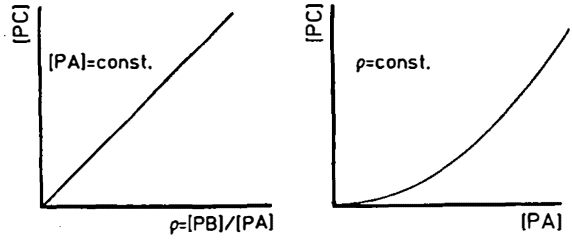
At this moment, a large number of systems which form interpolymer complexes is known. We classify them as weak and strong complexes [3]. In general, the polymer complex concentration [PC] or any property directly related to it, at constant polybase/polyacid mole ratio, $\rho = [PB]/[PA]$, is proportional to $[PA]^{\nu}$. In a simplified scheme, for a weak PC

$$[PC] = K\,[PA]\,[PB] = K\,\rho\,[PA]^2 \qquad (1)$$

a) Part 1: cf. ref. [3]

b) IUPAC name of itaconate: 2-methylenesuccinate.

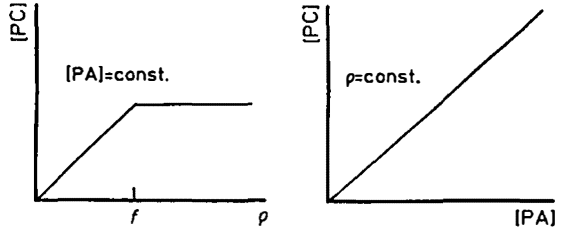
Scheme 1: Weak polymer-complex



where K represents the equilibrium constant for the formation of the PC and it is assumed that [PC] is so small that the initial concentrations can be taken for both, [PA] and [PB]. ν is therefore equal to 2 for weak PC's and a parabolic curve of a PC-dependent property vs. [PA] at $\rho = 1$ must be expected[3] (see Scheme 1). Such a behavior was observed for the system here studied (see ref.[3]).

For strong PC's, two different situations must be considered: a) $\rho < f$ where f is the stoichiometric ratio PB:PA in the PC and b) $\rho > f$. In the latter case, [PC] = [PA] since PB is in excess with respect to the stochiometric ratio and it is assumed that the equilibrium is totally shifted to the formation of PC. In the former case, [PC] = [PB] = ρ [PA] because PA is in excess. In both cases $\nu = 1$, i.e. keeping ρ constant at any value below or above f, and changing [PA], then [PC] or any property directly related to it changes proportionally. On the other hand, keeping [PA] constant and increasing ρ, [PC] increases linearly for low ρ values and levels off for ρ larger than f (see Scheme 2). This behaviour can be observed in several systems previously published. For example: poly(acrylic acid)/poly(4-vinylpyridine) in 50 vol.-% water-methanol[4], poly(acrylic acid)/poly(*N*,*N*-dimethylacrylamide-*co*-acrylamide) in water[5], poly(methacrylic acid)/poly(*N*-vinyl-2-pyrrolidone)[6], poly(acrylic acid)/poly(oxyethylene) in water[7] and poly(methacrylic acid) partially ionized/poly(oxyethylene) in water[8].

Scheme 2: Strong polymer-complex



ρ=[PB]/[PA]; *f*: stoichiometric ratio PB:PA in the complex

In this paper we study a weak PC formed by poly(monobenzyl itaconate) (PMBI) and poly(*N*-vinyl-2-pyrrolidone) (PVP) in methanol (MeOH)[3]. We have peviously

found that, to get reproducible measurements on this PC, it was necessary to prepare it always with the same protocol. The objective of this work is to determine the reason for that.

It was previously shown[9] that, in some cases, the complex formed directly after mixing has an unstable non-equilibrium structure that may turn into a more stable form with time, by heating, by cooling, within a velocity gradient, etc. All these possibilities will be analyzed in the system here considered.

The turbidity (τ) of the PC solutions was chosen in order to study the above mentioned phenomena. In accordance with Mie theory[10,3], the expression for the turbidity at wavelength λ (i.e. $-$ (ln T)/l, with T = transmittance and l = layer thickness of the solution) is as follows

$$\tau(\lambda) = \frac{4c\pi^4}{d} \cdot \left[\frac{\tilde{n}^2-1}{\tilde{n}^2+2}\right]^2 \cdot \frac{\overline{D_6} \cdot n_1^4}{\overline{D_3} \cdot \lambda_0^4} \qquad (2)$$

where n_1 is the refractive index of the solvent, c is the concentration of scattering particles in g/cm^3, d is their segmental density (i.e. the reciprocal of intrinsic viscosity), $\tilde{n}$ is the particle to solvent refractive-index ratio, λ_0 the wavelength of the incident light in vacuom and $\overline{D_i}$ represents the i-th moment of the particle-diameter distribution. We have found[3] that plots of τ vs. λ_0^{-4} are linear for the range of wavelengths studied (600–400 nm), therefore, Eq. (2) can be simplified to

$$\tau(\lambda) = S\,\lambda_0^{-4} = \frac{24\,\pi^3\,V\,c}{d} \cdot \left[\frac{\tilde{n}^2-1}{\tilde{n}^2+2}\right]^2 \cdot n_1^4 \cdot \lambda_0^{-4} \qquad (3)$$

where λ is the wavelength in solution, V is the weight-average volume of the scattering particles (assuming they are spherical), and S represents a constant (= $\tau\,(\lambda_x)/\lambda_x^4$, where λ_x is any arbitrary wavelength). The PC refractive index can be considered to be constant and can be estimated as the average of the refractive index of both PMBI and PVP [n (PMBI)[11] = 1,58, n (PVP)[12] = 1,53]. That makes $\tilde{n}$ = n(PC)/n(MeOH) = 1,17. Therefore, S is proportional to PC concentration and volume and depends inversely on its segmental density. The dependence of S on those variables for a PMBI-PVP complex has been previously studied[3].

Experimental part

Four samples of poly(*N*-vinyl-2-pyrrolidone) (PVP) (from Aldrich) were used: PVP10, PVP24, PVP40 and PVP360. Their weight-average molecular weights given by the supplier, were $1{,}0 \cdot 10^4$, $2{,}4 \cdot 10^4$, $4{,}0 \cdot 10^4$ and $3{,}6 \cdot 10^5$, respectively.

Poly(monobenzyl itaconate) (PMBI) was synthesized by radical polymerization[13] and fractionated[13]. Two atactic[14] samples, whose viscosity-average molecular weights were $3{,}8 \cdot 10^4$ and $5{,}4 \cdot 10^4$, were used in this work. The first one was used except where indicated.

Methanol of RS quality spectral grade was purchased from Carlo Erba.

Turbidimetric measurements were performed on a Shimadzu UV-240 spectrophotometer. The temperature in the sample holder was controlled by means of a Lauda RM-6 thermocirculating bath.

Polymer complex (PC) solutions were obtained by mixing methanol and solutions of PVP and PMBI in methanol in different proportions. After preparing the samples, they were shaken vigorously and left for some minutes before performing any measurement. Further details about the order of addition and concentrations of stock solutions will be given below. A sonication bath from Selecta was used at a fixed frequency.

Results and discussion

Samples of ternary polymer-polymer-solvent systems are usually prepared by mixing two polymer stock solutions and solvent in different proportions. Systems which form strong complexes like poly(4-vinylpyridine)/poly(acrylic acid) in methanol (MeOH)[4], react instantaneously and any change in the protocol of preparing the samples does not modify the results of common measurements. That is not the case for a weak complex like the one studied here.

In the following, we will show how changes in the order of addition of stock solutions, their concentration, and other factors like aging time, sonication and changes in temperature modify the turbidity of PC solutions.

Order of addition

The effect of the order of addition of stock solutions has been studied for two sets of experiments the results and initial conditions of which are summarized in Tab. 1. In Fig. 1 we show the spectra of three identical samples, prepared with three different orders of addition, in terms of optical density as a function of λ_0 (turbidity is related to optical density by $\tau = O.D. \cdot 2{,}303$).

The main feature of Tab. 1 is that a different sequencce in the addition of polymer pattern solutions and solvent produces a very different value of S when the initial concentrations of PMBI or PVP are relatively high. The highest value of S was obtained when both polymers were mixed in concentrated solution ($[PMBI]_0 = [PVP]_0 =$

Tab. 1. Wavelength-independent turbidity, S, as a function of the order of mixing of two stock solutions of PMBI[a] and PVP[b] and of methanol (MeOH). Weight-average molecular weights of the used PVP samples, $\bar{M}_{PVP}$, concentrations of stock solutions (subscript 0), PMBI concentration after mixing (subscript f) and $\rho = [PVP]_f/[PMBI]_f$ are included

$\bar{M}_{PVP}$ (sample)	$[PMBI]_0$ / mol · L^{-1}	$[PVP]_0$ / mol · L^{-1}	$[PMBI]_f$ / mol · L^{-1}	ρ	Order of mixing	$S \cdot 10^{-9}$ / nm^3
$1 \cdot 10^4$ (PVP10)	0,1	0,1	$3{,}0 \cdot 10^{-3}$	1	PVP + PMBI + MeOH	58
					MeOH + PVP + PMBI	35
					PMBI + MeOH + PVP	6
$4 \cdot 10^4$ (PVP40)	$1{,}2 \cdot 10^{-2}$	$8{,}8 \cdot 10^{-3}$	$4{,}1 \cdot 10^{-3}$	0,7	PMBI + PVP + MeOH	3
					PMBI + MeOH + PVP	2
					PVP + MeOH + PMBI	2

[a] PMBI: Poly(monobenzyl itaconate).
[b] PVP: Poly(*N*-vinyl-2-pyrrolidone).

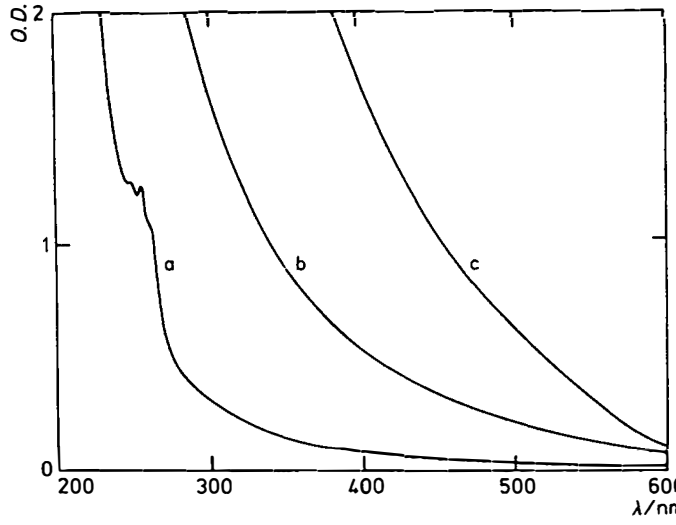


Fig. 1. Absorption spectra (optical density vs. wavelength) of polymer-complex solutions prepared with PVP10 for three different orders of addition: (a) PMBI + MeOH + PVP, (b) MeOH + PVP + PMBI and (c) PVP + PMBI + MeOH. ρ = 1, $[PMBI]_0 = [PVP]_0$ = 0,1 mol · L^{-1} and $[PMBI]_f = 3{,}0 \cdot 10^{-3}$ mol · L^{-1} (Symbols and abbreviations see Tab. 1)

0,1 mol · L^{-1}) and solvent was added at the end of the process. If the concentrated PVP solution was added to the diluted PMBI solution, S got the lowest value. Thus, we can conclude that the local concentration in the mixing process is the factor controlling the PC formation better than the final concentration of polymers. The PC is therefore formed in a metastable state and not in an equilibrium state and it seems that the polyacid (PMBI) nucleates the PC particles: high local PMBI concentrations are needed to get high S values, but high PVP local concentrations do not have the same effect.

Concentration of the initial stock solutions

The results of this experiment are shown in Tab. 2. The initial PMBI concentration $[PMBI]_0$ was varied in the range $1{,}3 \cdot 10^{-2}$ – $2{,}0 \cdot 10^{-1}$ mol · L^{-1} while $[PVP]_0$ and the concentrations after mixing, $[PVP]_f$ and $[PMBI]_f$, were kept constant and equal to $4{,}0 \cdot 10^{-3}$ mol · L^{-1}, $2{,}0 \cdot 10^{-3}$ mol · L^{-1} and $2{,}0 \cdot 10^{-3}$ mol · L^{-1}, respectively. The order of addition was the same in any case: PVP + PMBI + MeOH.

It can be seen in Tab. 2 that in the low concentration range ($[PMBI]_0 < 2{,}5 \cdot 10^{-2}$ mol · L^{-1}) S is almost independent of $[PMBI]_0$, but when the $[PMBI]_0$ concentration is raised, S increases abruptly. Since the final PMBI concentration is the same for all cases shown in Tab. 2, it may be confirmed that it is the local PMBI concentration in the drop of PMBI solution in the instant of mixing both polymers, and not the overall PMBI concentration which controls the formation of non-equilibrium PC particles. Changes in $[PVP]_0$ in the range $2{,}5 \cdot 10^{-2}$ — $1{,}0 \cdot 10^{-1}$ mol · L^{-1}, keeping constant

Tab. 2. Wavelength-independent turbidity, S, as a function of the concentration of the polyacid stock solution, $[PMBI]_0$. $[PVP]_0 = 4{,}0 \cdot 10^{-3}$ mol · L^{-1}; $[PMBI]_f = [PVP]_f = 2{,}0 \cdot 10^{-3}$ mol · L^{-1}. Order of mixing: PVP10 + PMBI + MeOH (Symbols and abbreviations see Tab. 1)

$[PMBI]_0$ in mol · L^{-1}	$S \cdot 10^{-9}$ in nm^3
$1{,}3 \cdot 10^{-2}$	7
$2{,}5 \cdot 10^{-2}$	6
$1{,}0 \cdot 10^{-1}$	18
$2{,}0 \cdot 10^{-1}$	24

$[PMBI]_0$, $[PMBI]_f$ and $[PVP]_f$ ($2{,}5 \cdot 10^{-2}$ mol · L^{-1}, $4{,}0 \cdot 10^{-3}$ mol · L^{-1} and $4{,}0 \cdot 10^{-3}$ mol · L^{-1}, respectively) gave place to changes of S smaller than the experimental error. This result may confirm the role of the polyacid as a nucleus of the PC particles.

Aging time

The time stability of the PC specimens has been qualitatively checked measuring the turbidity of the PC solutions after a long period of time (t_∞ = 8 months, stored at room temperature). Aging times of the order of hours gave no measurable change of S.

Two sets of experiments were carried out. In the first one (set A) the tubidity at t_∞ was compared with the original, i.e. the turbidity at time zero, $\tau(t_0)$, for solutions in which $[PMBI]_f$ was varied keeping ρ constant ($\rho = [PVP]_f/[PMBI]_f$). In the second set (set B), $[PMBI]_f$ was kept constant and ρ was varied in a broad range. In both sets, the order of adddition was PMBI + MeOH + PVP.

Results concerning set A are presented in Fig. 2 and Fig. 3. In Fig. 2, S at t_0 and t_∞ is plotted as a function of $[PMBI]_f$ for PVP10 and PVP24. Several comments can be made: for both PVP samples, S increases with time. The curves for both PVP samples overlap at t_0 but they are shifted to t_∞. In both PVP samples, the highest absolute change in S corresponds to the highest PMBI concentration, although the relative change is similar for the whole range of PMBI concentrations: around 70% for the PVP24 serie and 300% for the PVP10 one. Finally, we remark that the last three points in Fig. 2 for PVP10 fraction could not be measured at t_∞ because phase separation took place in between. Changes in S may be interpreted in terms of evolution of the system to an equilibrium state.

In Fig. 3, double-logarithmic plots of S as a function of $[PMBI]_f$ are presented. The results at t_0 can be fitted to straight lines with slopes around 2 (Tab. 5). At t_∞, the results can also be fitted to straight lines (with good correlation coefficients), the slopes of which are very close to the former, but slightly smaller (Tab. 5).

The behaviour observed in the second set of experiments (set B, in which polybase/polyacid mole ratio, ρ, was varied) depends on the molecular weight of PVP. Results for two PVP samples (PVP24 and PVP360) are presented in Tab. 3. For PVP24 at t_∞, the dependence of S on ρ remained essentially the same as for t_0. The sample with the highest molecular weight (PVP360) presented almost no change of S with time at any ρ value.

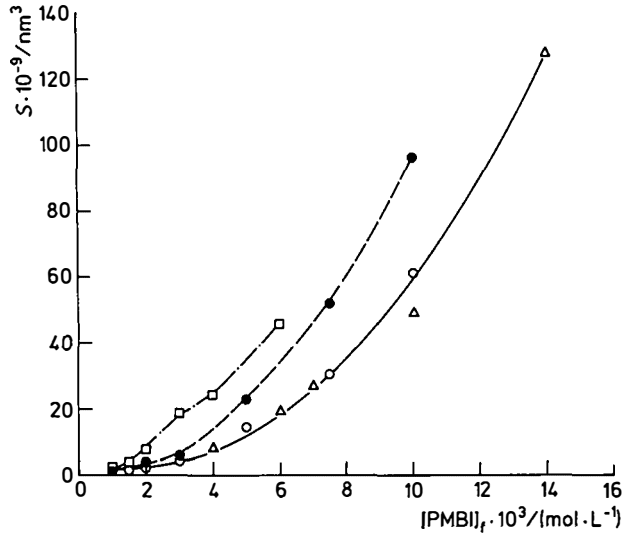


Fig. 2. Wavelength-independent turbidity, S, as a function of $[PMBI]_f$ for polymer-complex solutions in the moment of preparation (t_0) and eight months later (t_∞) for two different PVP samples: (○): PVP24 (t_0); (●): PVP24 (t_∞); (△): PVP10 (t_0) and (□): PVP10 (t_∞). $\rho = 1$ (Symbols and abbreviations see Tab. 1)

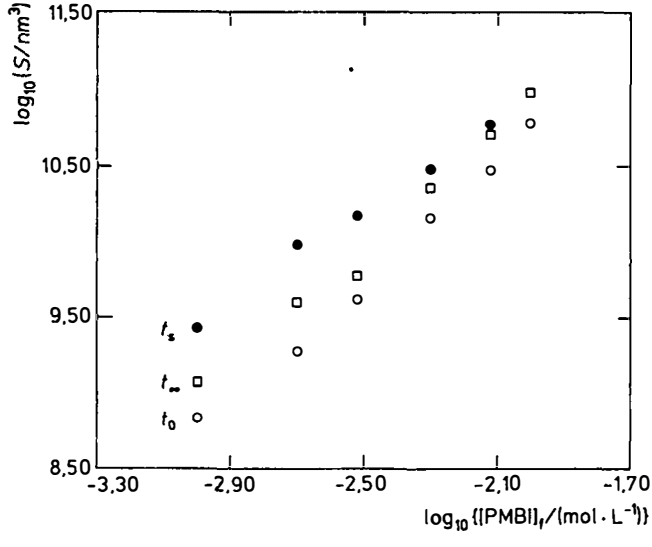


Fig. 3. Double-logarithmic plots of S vs. $[PMBI]_f$ at t_0, t_∞ and after 37 min sonication (t_s) for PC solutions with PVP24 (Symbols and abbreviations see Fig. 2)

Tab. 3. Wavelength-independent turbidity, S, as a function of aging time for two samples with different molecular weights, $\bar{M}_{PVP}$, and as a function of ρ. $[PMBI]_f$ was kept constant. Subscript 0 refers to the initial complex and subscript ∞ to eight months later (Symbols and abbreviations see Tab. 1)

$\bar{M}_{PVP}$ (sample)	$\frac{[PMBI]_f}{mol \cdot L^{-1}}$	ρ	$\frac{S_0 \cdot 10^{-9}}{nm^3}$	$\frac{S_\infty \cdot 10^{-9}}{nm^3}$
$3{,}6 \cdot 10^5$ (PVP360)	$6{,}3 \cdot 10^{-3}$	0,0	0	2
		1,0	34	35
		5,2	27	31
		10,4	20	20
$2{,}4 \cdot 10^4$ (PVP24)	$6{,}3 \cdot 10^{-3}$	0,0	0	2
		0,5	19	27
		1,5	22	28
		5,0	20	33
		10,0	62	64

To summarize, eight months are needed to observe changes in S of some systems but in any case, the dependence of S on ρ (at constant $[PMBI]_f$ or with $[PMBI]_f$ (at constant ρ) does not change appreciably. Thus, time evolution of the system is always very slow and depends on the sample characteristics.

Effect of the temperature

The temperature stability of the PC solutions has been checked by measuring the turbidity at a fixed wavelength (λ = 420 nm in which no absorption of either PVP or PMBI occurs). PC solutions were obtained by mixing stock solutions, with concentrations $[PMBI]_0 = 5{,}9 \cdot 10^{-2}$ mol $\cdot$ L^{-1} and $[PVP]_0 = 1{,}1 \cdot 10^{-2}$ mol $\cdot$ L^{-1}, to give the same final PMBI concentration ($[PMBI]_f = 5{,}9 \cdot 10^{-3}$ mol $\cdot$ L^{-1}) for different ρ values. The temperature was varied in the range 10–50 °C, the latter being the upper limit just below the solvent boiling point. Samples were kept at least 15 min at each temperature before measurement.

Results of turbidity, τ, as a function of temperature, T, are presented in Fig. 4. In this figure, the data can be fitted to straight lines with very small slopes ($\approx 10^{-4}$ °C^{-1}). This behaviour suggests that high temperatures do not modify appreciably the state of PC particles.

Some experiments have also been carried out keeping PC solutions at −5 °C for three days. S values remained constant after this cooling process for solutions in which $\bar{M}_{PVP}$, $[PMBI]_f$ and ρ were varied. The slopes of the double-logarithmic plots of S vs. $[PMBI]_f$ do not vary appreciably as can be seen in Tab. 5.

Effect of sonication

In samples used for this experiment, $[PMBI]_f$ ranged between 10^{-3} mol $\cdot$ L^{-1} and $7{,}5 \cdot 10^{-3}$ mol $\cdot$ L^{-1} (ρ = 1 in any case). They were immersed in a sonication bath and their turbidity was measured after 7, 17 and 37 min.

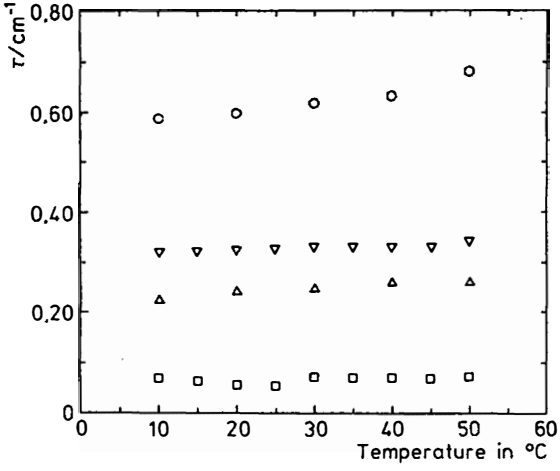


Fig. 4. Turbidity, τ, vs. temperature for several polymer complex solutions with different ρ: (□): ρ = 0,28; (△): ρ = 0,47; (▽): ρ = 0,94 and (○): ρ = 1,41. Molecular weights: $\bar{M}_{PMBI}$ = $5{,}4 \cdot 10^4$, $\bar{M}_{PVP}$ = $3{,}6 \cdot 10^5$ and $[PMBI]_f$ = $5{,}9 \cdot 10^{-3}$ mol · L^{-1} (Symbols and abbreviations see Tab. 1)

Tab. 4. Wavelength-independent turbidity, S, as a function of sonication time (subscripts i, a, b and c correspond to: initial value, 7, 17 and 37 min of sonication) for two experiments with different $\bar{M}_{PVP}$ and $[PMBI]_f$. ρ = 1 was kept constant (Symbols and abbreviations see Tab. 3)

$\bar{M}_{PVP}$ (sample)	$[PMBI]_f \cdot 10^3$ / mol · L^{-1}	$S_i \cdot 10^{-9}$ / nm^3	$S_a \cdot 10^{-9}$ / nm^3	$S_b \cdot 10^{-9}$ / nm^3	$S_c \cdot 10^{-9}$ / nm^3
$2{,}4 \cdot 10^4$ (PVP24)	1,0	1,2	2,0	2,4	2,7
	2,0	4,9	6,8	8,3	9,5
	3,0	7,4	11,0	11,7	15,1
	5,0	23,5	28,1	28,1	30,2
	7,5	—	57,9	61,0	60,0
$1{,}0 \cdot 10^4$ (PVP10)	1,0	1,8	2,1	2,5	2,2
	1,5	3,4	3,7	3,3	3,5
	2,0	8,0	9,9	10,9	12,0
	3,0	18,4	18,3	19,4	18,2
	4,0	26,2	26,0	25,5	26,5
	6,0	46,8	45,0	44,4	48,5

Results are presented in Tab. 4. The general behaviour which can be observed for PVP24 is that, at short times, turbidity increased with sonication time. Above 7 min, the S values remained nearly constant with a slight tendency to increase. The absolute changes in S are higher for the higher PMBI concentrations but the relative changes of S show the opposite tendency, i. e. they are higher for the lower concentrations.

For PVP10, the behaviour is not so clear. In some cases a slight increase in S was observed, but as a general rule, the turbidity stayed constant for all sonication times. Thus, some samples are closer to the equilibrium than others, depending on the molecular weight of PVP.

Data of the slopes, ν, obtained from double-logarithmic plots of S vs. $[PMBI]_f$ after sonication, are collected in Tab. 5. The results obtained for aging time and cooling treatments are also included. A perceptible evolution of the ν value can be detected for both PVP samples, but two different limits were reached: for PVP24, ν decreased continously to around 1,5, while for PVP10, ν remained almost constant ($\approx 1{,}7-1{,}8$) for any sonication time.

Tab. 5. Changes of the exponent ν ($S \sim [PMBI]^{\nu}$) with aging time, cooling and sonication: ν_0, initial value: ν_∞, after 8 months; ν_c, after cooling at $-5\,°C$ for three days and ν_s after 37 min sonication. The exponents are given for two samples of PVP with different molecular weights $\bar{M}_{PVP}$ (Symbols and abbreviations see Tab. 1)

$\bar{M}_{PVP}$	ν_0	ν_∞	ν_c	ν_s
$2{,}4 \cdot 10^4$	1,97	1,92	1,79	1,49
$1{,}0 \cdot 10^4$	1,98	1,80	1,89	1,77

Values of ν close to two indicate that a weak PC is formed whereas ν values close to one indicate that the PC is strong. The decrease of ν (Tab. 5) with different treatments indicates that the PC is becoming stronger, i. e. polymer-polymer interactions substitute progressively polymer-solvent contact points. According to Tab. 5, sonication is the most efficient process to bring the PC to the final equilibrium state, and it is easier for PVP24 than for low-molecular-weight PVP (PVP10).

Conclusions

The turbidity of polymer-complex (PC) solutions, formed directly after mixing of methanolic solutions of PMBI and PVP, depends on the local concentration of the polyacid suggesting that PMBI nucleates the PC formation. In some conditions the PC formed is metastable and the treatment that turns it most quickly to the equilibrium is sonication. In any case, the PC evolution is reflected by an increase in S and a decrease in ν, the latter showing stonger polymer-polymer interactions.

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[1] E. A. Bekturov, L. A. Bimendina, *Adv. Polym. Sci.* **45**, 99 (1981);
E. Tsuchida, K. Abe, *Adv. Polym. Sci.* **45**, 1 (1982)
[2] J. Y. Lee, P. C. Painter, M. Coleman, *Macromolecules* **21**, 954 (1988);
P. C. Painter, Y. Park, M. Coleman, *Macromolecules* **22**, 570 (1989);
J. N. G. Cowie, M. T. Garay, D. Lath, I. J. McEwen, *Br. Polym. J.* **21**, 81 (1989)
[3] A. Pérez-Dorado, I. F. Piérola, J. Baselga, L. Gargallo, D. Radic, *Makromol. Chem.* **190**, 2975 (1989)

[4] I. F. Pierola, M. Cáceres, P. Cáceres, M. A. Castellanos, J. Nuñez, *Eur. Polym. J.* **24**, 895 (1988)
[5] Y. Wang, H. Morawetz, *Macromolecules* **22**, 164 (1989)
[6] H. Ohno, K. Abe, E. Tsuchida, *Makromol. Chem.* **179**, 755 (1978)
[7] I. Iliopoulos, R. Audebert, *Polym. Bull. (Berlin)* **13**, 171 (1985);
I. Iliopoulos, R. Audebert, C. Quivoron, *"Reversible Polymer Gels and Related Systems"*, ed. by P. S. Russo, ACS Symposium Series, 1987;
J. J. Heyward, K. P. Ghiggino, *Macromolecules* **22**, 1159 (1989)
[8] H. T. Oyama, D. J. Hemker, C. W. Frank, *Macromolecules* **22**, 1255 (1989)
[9] E. Tsuchida, Y. Osada, K. Abe, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 767 (1976);
E. Tsuchida, *Makromol. Chem.* **175**, 603 (1974);
E. Tsuchida, K. Abe, M. Honma, *Macromolecules* **9**, 112 (1976)
[10] M. Kerker, *"The Scattering of Light and Other Electromagnetic Radiations"*, Academic Press, New York 1969
[11] I. Hernandez-Fuentes, *private communication*
[12] *"Polymer Handbook"*, ed. by J. Brandup, E. H. Immergut, 2nd ed., Wiley, New York 1975
[13] M. Yazdani-Pedran, L. Gargallo, D. Radic, *Eur. Polym. J.* **21**, 707 (1985)
[14] A. Horta, I. Hernández-Fuentes, L. Gargallo, D. Radic, *Makromol. Chem., Rapid Commun.* **8**, 523 (1987)